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Preliminary communication

FORMATION OF THE NOVEL BIS(DIPHENYLPHOSPHINO)METHANIDE LIGAND BY DEPROTONATION OF A COORDINATED BIS(DIPHENYLPHOSPHINO)METHANE. CRYSTAL AND MOLECULAR STRUCTURE OF CHLORO-TRIETHYLPHOSPHINE-BIS(DIPHENYLPHOSPHINO)METHANOPLATINUM(II)

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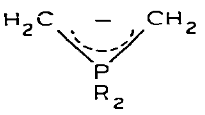
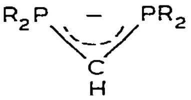
Summary

$[PtCl(PEt_3)(Ph_2PCHPPh_2)]$, a complex containing the bis(diphenylphosphino)methanide ligand, has been synthesized by reaction of NaH with $[PtCl(PEt_3)(Ph_2PCH_2PPh_2)]^+$ and characterized by ^{31}P NMR and X-ray crystallography.

There has been intense recent interest in complexes of deprotonated phosphorus ylids, I [1]. In contrast, the alternate ligand system, II, has been little studied despite the demonstration in 1972 that palladium complexes, $[Pd_2Cl_2\{CH(PPh_2)_2\}_2]$ and $[Pd_2(\eta^3\text{-}C_3H_5)_2\{CH(PPh_2)_2\}_2]$, are accessible via reactions of $Li[CH(PPh_2)_2]$ [2].



(I)



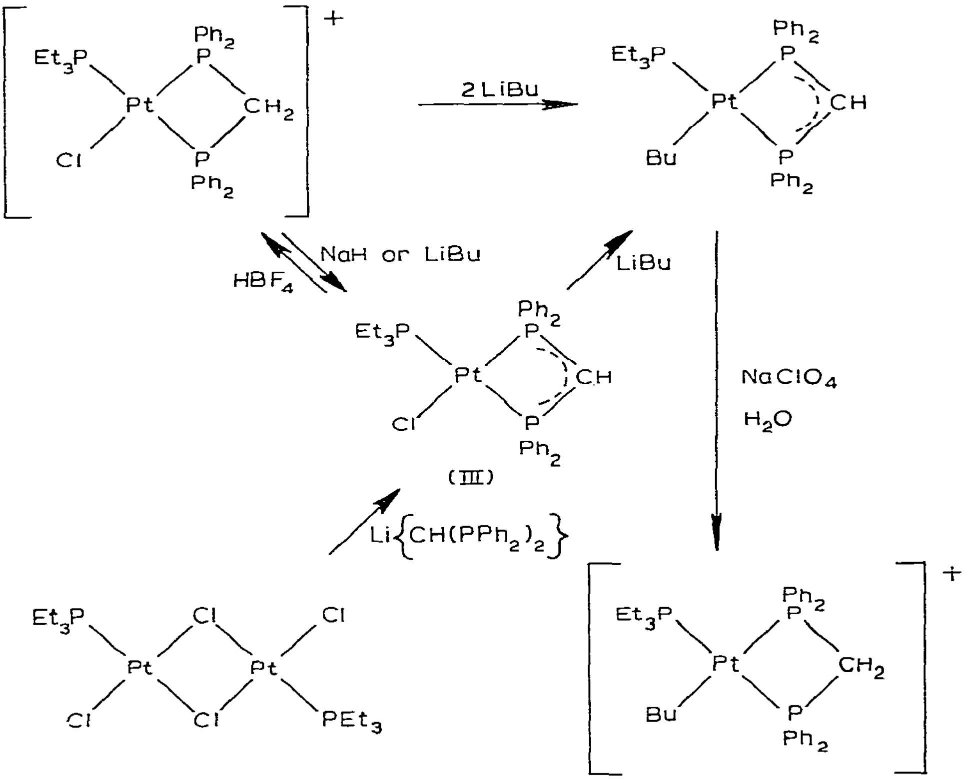
(II)

The original palladium compounds were insoluble and difficult to characterize and, except for structural study of a complex, trimeric Cu^I derivative involving bonding of P and C to different Cu atoms [3], the chemistry of type II ligands has remained unexplored. Very recently [4], a development of the palladium chemistry has been reported using reactions of $[MCl_2(PMe_3)_2]$, M = Ni, Pd, Pt, with $Li[CH(PPh_2)_2]$. The initial products, $[M\{CH(PPh_2)_2\}_2]$, are again intractable but subsequent reaction with a phosphonium ylid, $(CH_3)_3PCH_2$, yields crystallizable products, $[M\{CH(PPh_2)_2\}\{(CH_3)_2P(CH_2)_2\}]$, containing ligands of both types I and II [4].

We wish to report that formation of type II ligands is much more easily achieved by direct deprotonation of a coordinated bis(diphenylphosphino)-methane. Thus, reaction of [PtCl(PEt$_3$)(Ph$_2$PCH$_2$PPh$_2$)] [BF$_4$] with NaH in tetrahydrofuran solution under mild conditions gives a high yield of [PtCl(PEt$_3$)(Ph$_2$PCHPPh$_2$)], III, as air-stable, yellow crystals. Moreover, the presence of only Cl and PEt$_3$ as supporting ligands, rather than the unusual phosphonium bis(methylide) system, indicates that the type II ligand has no special requirements for stability. An extensive chemistry may be anticipated and is currently under investigation. The reactions shown in Scheme 1 have been established by microanalysis and ^{1}H and ^{31}P NMR studies of the various products and all proceed in high yield. It is especially noteworthy that even LiBu, which is expected to be less selective than NaH, attacks [PtCl(PEt$_3$)-(Ph$_2$PCH$_2$PPh$_2$)]$^+$ initially at the chelate ligand methylene group rather than at the Pt—Cl bond.

SCHEME 1

PREPARATION AND REACTIONS OF BIS(DIPHENYLPHOSPHINO)METHANIDE COMPLEXES



^{31}P NMR spectra of all the chelate complexes shown in Scheme 1 belong to the ABX spin system (A = B = PPh$_2$, X = PEt$_3$) and have side bands attributable to coupling to ^{195}Pt (I = 1/2, abundance = 33.8%). All assignments have been verified using computer simulation with the UEAITR programme [5] and the parameters indicate that the deprotonation reaction introduces only a

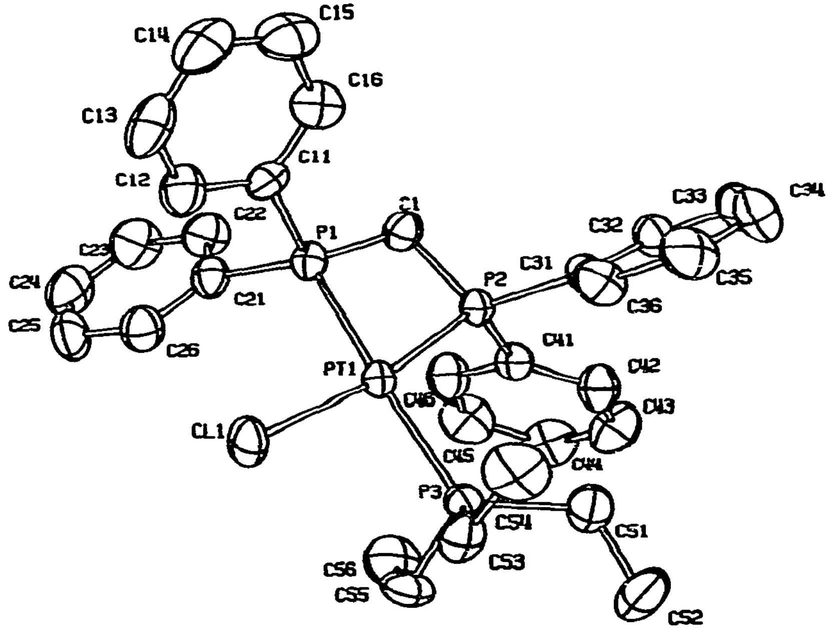


Fig. 1. The molecular structure of [PtCl(PEt$_3$)(Ph$_2$PCHPPh$_2$)].

small perturbation of the platinum—phosphorus bonding. For example, using the labelling from Figure 1; ^1J(Pt—P(1)) in [PtCl(PEt$_3$)(Ph$_2$PCHPPh$_2$)] is +1797 Hz, ^1J(Pt—P(2)) +2853 Hz, ^1J(Pt—P(3)) +2400 Hz, ^2J(P(1)—P(3)) +397 Hz, ^2J(P(1)—P(2)) ±44.5 Hz, ^2J(P(2)—P(3)) −3.3 Hz. Corresponding parameters for [PtCl(PEt$_3$)(Ph$_2$PCH$_2$PPh$_2$)]$^+$ are +1864, +3042, +2333, +396, ±64.9 and −10.6 Hz, respectively.

A sample of [PtCl(PEt$_3$)(Ph$_2$PCHPPh$_2$)] was recrystallized from tetrahydrofuran/diethyl ether for X-ray study. Crystals were triclinic, space group $P\bar{1}$ with a = 1.2045(5), b = 1.3855(7), c = 1.0123(4) nm; α = 101.09(4)°, β = 98.08(6)°, γ = 111.24(6)°; Z = 2; D_m = 1.623, D_c = 1.617 g cm^{-3}. R = 0.032 at the present stage of anisotropic least squares refinement for 3844 independent reflections. An ORTEP plot of the molecular structure is shown in Figure 1. The geometry of the Pt—P(1)—C(1)—P(2) ring is similar to that recently reported for [Pt{CH(PPh$_2$)$_2$}{(CH$_3$)$_2$P(CH$_2$)$_2$}] [4] with these four atoms being close to co-planar (χ^2 = 20.5). In addition, the very low R value achieved in the present study has allowed us to locate the hydrogen atom on C(1) in a final difference map. This hydrogen also lies within 7 pm of the same plane. The two P—C(1) bonds are equal at 172 pm and the considerable shortening of these bonds relative to the other single P—C bonds in the structure (~183 pm) is clear evidence of multiple bonding. The Pt—P(1) and Pt—P(2) bond lengths are 231.7(2) and 225.2(2) pm, respectively, reflecting the differing *trans* influence of Cl and PEt$_3$. The bond angles P(1)—C(1)—P(2), 98.6(5)°, and P(1)—Pt—P(2), 69.65(8)°, are similar to those reported previously in both [Pt{CH(PPh$_2$)$_2$}{(CH$_3$)$_2$P(CH$_2$)$_2$}] [4], 95(1)° and 69.6(2)°, and [Pt(C$_6$H$_5$)$_2$-(Ph$_2$PCH$_2$PPh$_2$)] [6], 95° and 73°, respectively.

Thus the structural evidence clearly supports the formulation of the ligand as the anion, II, bonding as a bidentate chelate with C(1) relatively distant (299 pm) from the platinum. Moreover, the stability and geometry of this ligand is not dependent upon the presence of special supporting ligands. Further studies of the deprotonation route to this ligand are in progress with a variety of metal substrates.

Acknowledgement

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